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TRIPHENYL METHANE COMPOUNDS

BY

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THESIS

FOR THE

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IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ORIN BRADFORD GRANT

ENTITLED TRIPHENYL METHANE COMPOUNDS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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ACKNOWLEDGEMENT

I wish to express my sincere gratitude and appreciation to Dr. Roger Adams for the assistance and inspiration given me during the course of these experiments.

I.

INTRODUCTION

In spite of the fact that dyes of the triphenyl methane series are among those first known and at present have a very extended use, methods for their production are unsatisfactory, giving low yields and often their structure is misunderstood or even unknown. Hence, any work which will improve yields and throw light on the structure of these compounds will be welcomed by both the theoretical chemist and the dye plant enterpreneur.

The following work was undertaken with this object in view, with special emphasis on improvements in methods of producing Spirit Blue dyes. Direct synthesis was attempted, thus eliminating the possibility of the many side reactions so detrimental in the common process which is the phenylation of fuchsine.

II.

HISTORICAL

The first known artificial dyes were those of the triphenyl methane type and were discovered at approximately the same time, 1856-58 by chemists of England, France, and Germany. Nathanson is given priority, while Perkins, Hoffman, Roguencount and Dort follow in line.

Since then great strides have taken place in their manufacture, but due to the fact that owners keep their processes as secret as possible very little information has been published.

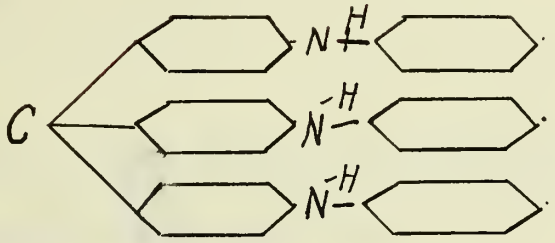
Girard and de Laire are accredited with the discovery of triphenyl rosaniline in 1862.

The method upon which the following work is based was discovered in 1892 by chemists of Geigy & Company, Basel, Switzerland. A patent of that year describes the process. Since then, no work has been published on it.

III.

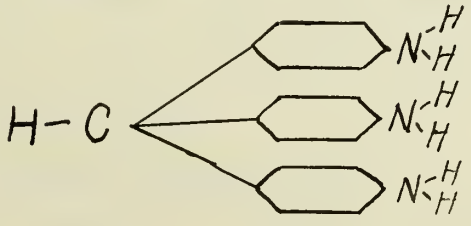
THEORETICAL CONSIDERATIONS

Spirit Blue is described in the literature as triphenylated rosaniline,

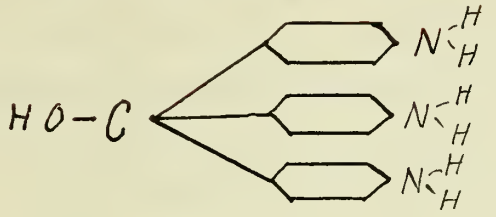


and Alkali Blue, Soluble Blue, and Water Blue as the mono, di, and trisulphonic acids respecively. The sulphonic group goes para to the amino group. More or less is to be found on methods of their preparation, but this is practically all that may be found on the struct of these compounds.

The common method of making Spirit Blue and its derivatives is to first prepare Fuchsine by heating a mixture of aniline, aniline hydrochloride, para toluidine, nitrobenzene, zinc chloride, and iron oxide at 160 degrees for twelve hours. The resulting low yields are readily understood when the complexity of this mixture is considered. First toluene is oxidized by the nitrobenzene to p-amino benzaldehyde. This in turn condenses with two mols of aniline to give the leuco base.



Upon further oxidation by the nitrobenzene this yields



which immediately forms Fuchsine with the hydrochloric acid present in the aniline hydrochloride.

It is highly improbable that all these reactions could take place simaltaneously in one mixture and give the best results. The importance of correct temperatures for various reactions is only too well known. Furthermore the presence or absence of acid, water, or catalyzer may promote one reaction and retard another. With all these in one mixture we have no method of control, which would make them function properly for each reaction.

Perhaps even more important than incomplete reactions are the formation of many undesirable products, so called side reaction products. In fact these make up the greater part of the product and represent at least 70% loss on the weight of the materials used.

The possible side reactions are too many to enumerate. It is sufficient to say that the finished Fuchsine melt contains only 12 to 15% pure color.

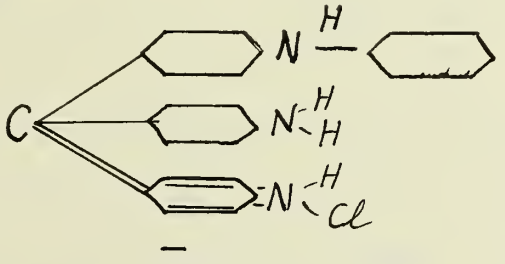
A typical analysis is:

Pure color	13%	Aniline oil	7%
Residue	55%	Moisture	25%

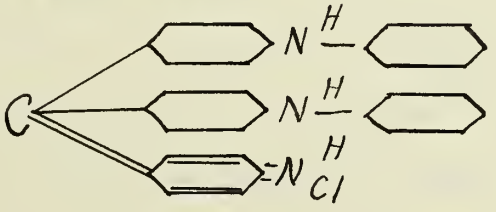
The formation of Rosaniline is easily accomplished by adding sodium hydroxide solution to a solution of Fuchsine. The reaction proceeds almost quantitatively.

Information on the chemistry of phenylation is entirely lacking. The literature merely states that when a mixture of Rosaniline and aniline are heated together with the proper catalyst, triphenyl rosaniline is formed. If this were the case, only one shade of blue could be obtained while in practice, shades ranging from a very reddish blue to a greenish blue are readily obtained by proper control of the reaction.

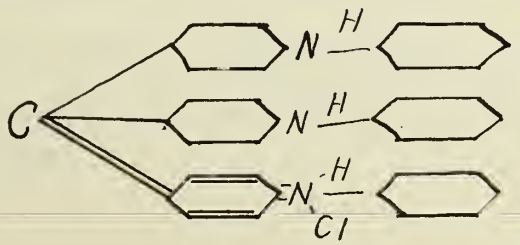
The various shades are merely different degrees of phenylation. Thus



is a very red shade blue,

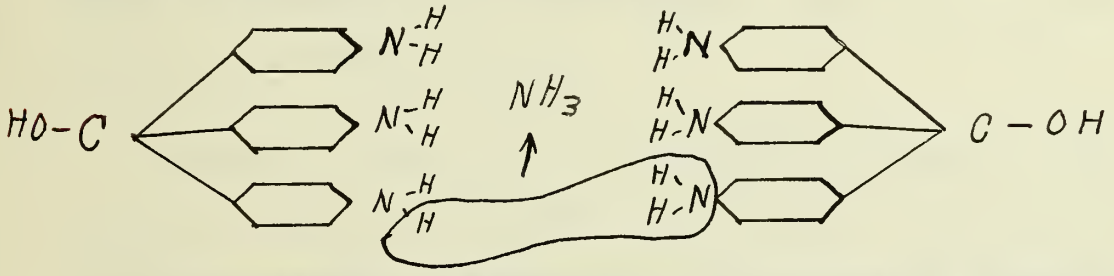


a pure blue and



a very green shade blue. Actually, the product is a mixture of the above and may be separated by their difference of solubilities in aniline hydrochloride. Even samples of the greenest shade blues are found to contain a very small amount of the monophenylated product.

Yields are fairly satisfactory, being 70 to 80% of theoretical. It is cut down by aniline reacting with itself to form diphenylomine and also Rosaniline molecules condensing with themselves.



The greatest disadvantage in this process is that the shade cannot be controlled. It is impossible to run diplicate melts which give identical shades. Furthermore, the greenest possible shade is not obtainable by this method, for the reason that the Rosaniline molecules will not react completely with aniline to form the triphenylated product. Some mono and diphenylated rosaniline is always present in the finished melt. Then too, the longer the reaction is carried out, the lower will be the yield and as the dye users demand a green shade, considerable loss occurs in prolonging the phenylation in order to obtain these green shades.

In view of these facts a synthesis which would give pure compounds would insure uniform shades and improve yields.

The sulphonation of Spirit Blue goes easily, inasmuch as 95% sulphuric acid is sufficiently strong to give any degree of sulphonation, vis. from a mono to a trisulphonated product. However, greatest care in temperature control and length of time must be exercised. Strict trade specifications require that the solubility in sulphuric acid solution be exact for the respective dyes Alkali, Soluble and Water Blues. Careful chemical control is necessary and even then many batches are oversulphonated.

Different shades require different lengths of time for sulphonation, also different proportions of acid to Spirit Blue. Prolonged sulphonation or too strong acid weakens the resulting dye.

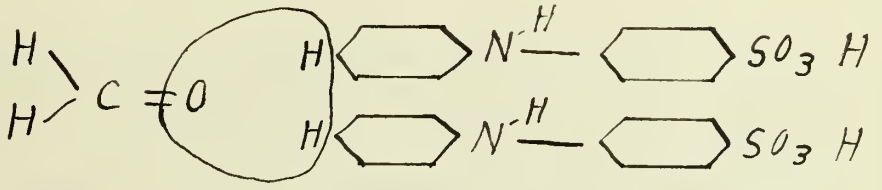
Thus it is seen that the many factors entering into sulphonation make the present method unsatisfactory.

In view of the fact that yields on Fuchsine are very low and accurate control of phenylation and sulphonation are impossible, the present method of production of Spirit Blue and its derivatives is very unsatisfactory.

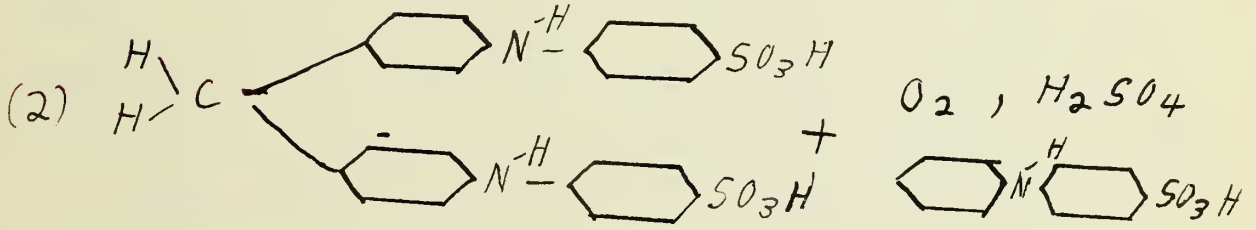
The possibilities of the new process have never been

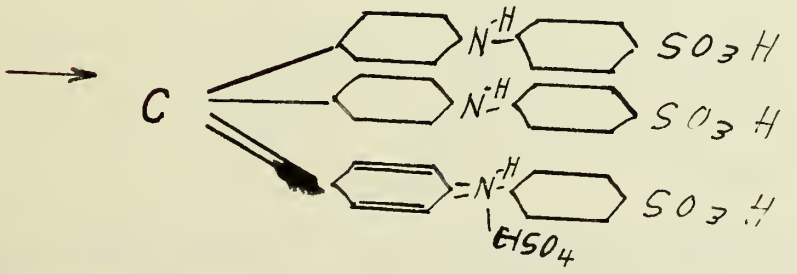
elaborated. A short description of the patent is the only information that can be found in the literature. The reactions are very simple. Two molicules of diphenylamine monosulphonic acid are condensed with formaldehyde and a third molecule of diphenylamine monosulphonic acid oxidized on the resulting ketone compound to form the dye.

(1)



(2)



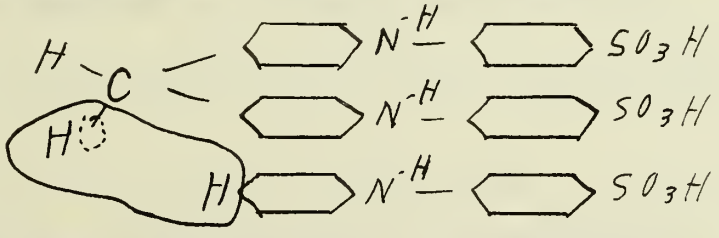


The reactions take place in two steps. Reaction one is the first step and the remainder of the reactions the second step.

The resulting product has a much greener shade than any product obtained from the old process and, as would be expected, is very soluble.

The conditions for this reaction are ideal. The possibilities of side reactions are very small. The sulphonic group makes the para hydrogen of the diphenylamine very reactive enabling the condensation to proceed very easily. No condensation agent is required. In fact, the presence of more than a very small amount of hydrochloric or sulphuric acids yields a hard insoluble product.

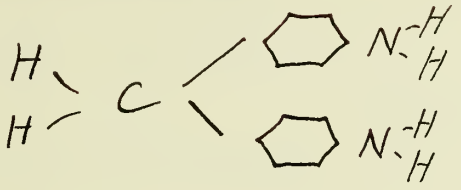
Again in the second step, the possibility of side reactions is neglegible. Thus in the reaction



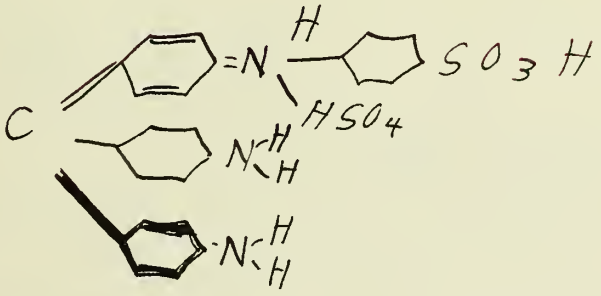
the third molecule of diphenylamine monosulphonic acid must go in the right place or not at all.

The most desired dye of the Spirit Blue series is Alkali Blue which contains only one sulphonic acid group. The red

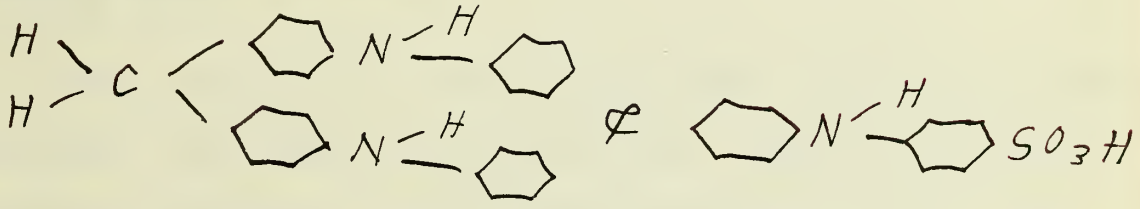
shade could be obtained by oxidizing a diphenylamine mono-sulphonic acid group on



giving

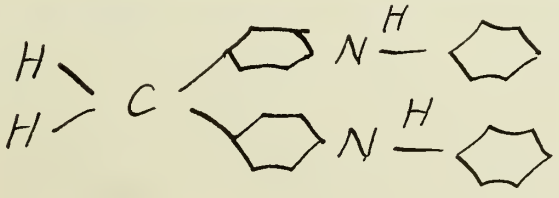


and the green shade from



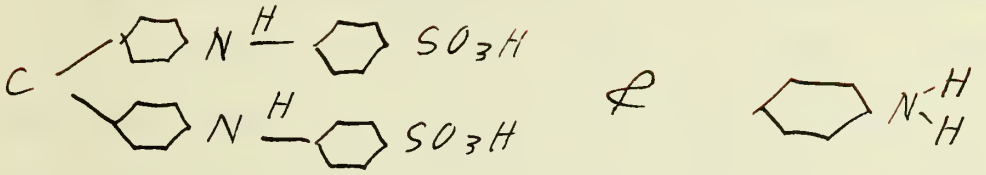
The intermediate blue shade could be made by mixing the red and green shades in the proper proportion.

In order to produce the green shade by the above method, the present low yield obtained in the preparation of

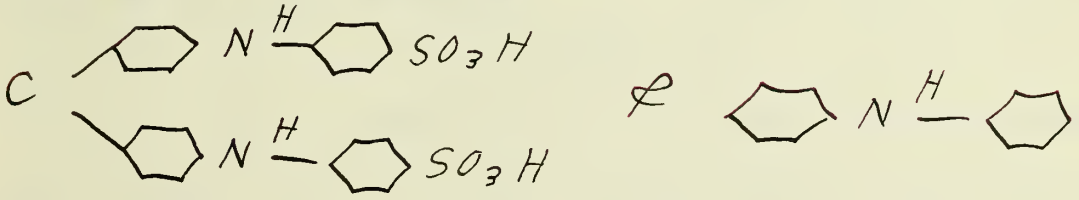


would have to be raised.

For Soluble Blue dyes



would give a blue shade and



a green shade.

The procedure for making Water Blue, the trisulphonated compound, has already been given above. Many other shades could be obtained by using dimethylaniline in various combinations.

Certain facts brought out in experiments with these dyes have demonstrated that much is to be learned about their structure. The colloidal nature of these compounds is shown in certain tests which the manufacturers make. The specifications of Alkali Blue for lithographic inks require that when two grams of the sample is dissolved in 100 cc. of water, it shall be precipitated with 1.3 cc. of ten times diluted 93% sulphuric acid. As the acid is

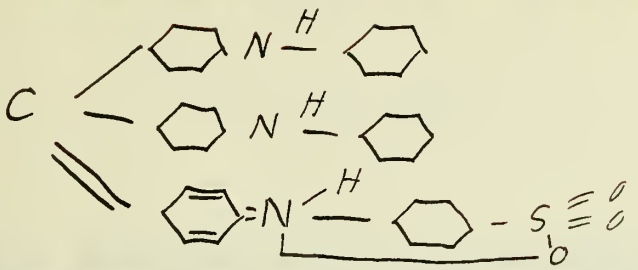
added, an extremely fine precipitate first appears, then as the end point is reached a heavy precipitate suddenly appears. If the solution is made up to 200 cc. instead of 100 cc., just twice as much acid is required to cause precipitation, showing that the concentration of the acid only is the determining factor. Soluble Blue (the disulphonic acid compound) requires about 17 cc. of the standard acid to cause precipitation. Water Blue cannot be precipitated with any amount of acid. A study of the colloidal nature of the various sulphonated blues should prove a valuable contribution to this branch of chemistry.

Varying conditions in the last steps of Akali Blue manufacture produce dyes which require more or less of the standard acid for their precipitation.

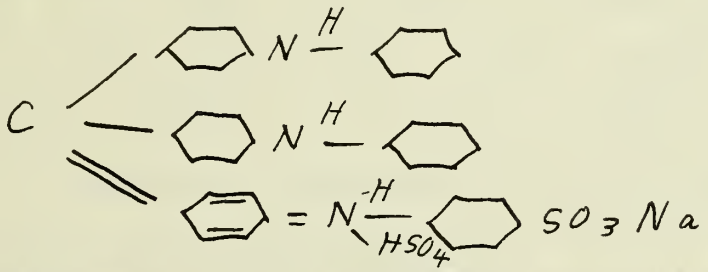
Sodium hydroxide is added to the free acid of Alkali Blue to form a soluble salt. If just sufficient alkali is added to render it soluble, 2.5 to 3.0 cc. of the standard acid is required for precipitation. If now more alkali is added so that the finished dye will contain approximately twice as much sodium, it will be precipitated with less than half the amount of acid than that required for the same dye containing less alkali.

The rate and temperature at which the Alkali Blue solution is evaporated also cause a marked change in the precipitation point. It would seem from the above that Alkali Blue possesses

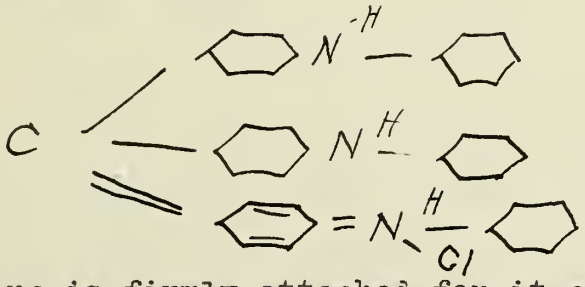
two structures. The one usually given is



From certain experimental facts and also the well established structure of the simpler triphenylmethane dyes it seems reasonable to believe that Alkali Blue possesses the following structure:

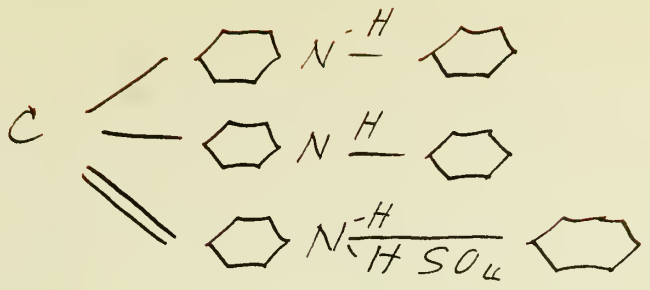


The structure for Spirit Blue from which Alkali Blue is derived is well established.

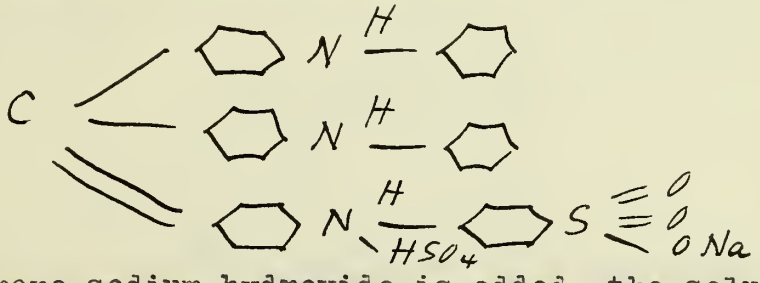


The chlorine is firmly attached for it can not be split off even with boiling sodium hydroxide.

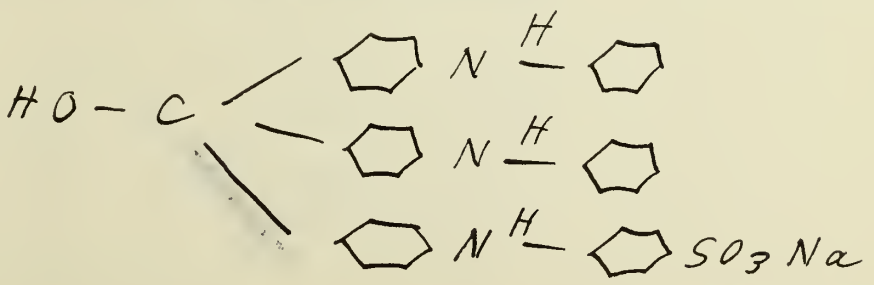
When concentrated sulphuric acid is added to this compound, hydrochloric acid is immediately given off. It seems logical to believe that the hydrochloric acid is merely displaced and that the sulphuric acid goes on in it place to give



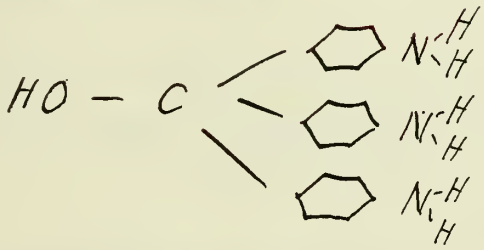
Upon continued action of the sulphuric acid, sulphonation takes place. The melt is then poured into water and washed acid free, and sodium hydroxide added until material is completely dissolved. If just enough sodium hydroxide is added, the product is completely soluble and is a deep blue color. It must possess the quinoid structure because it is colored. This is easily explained if we assume the hydrogen of the free sulphonic acid is replaced by the sodium to give



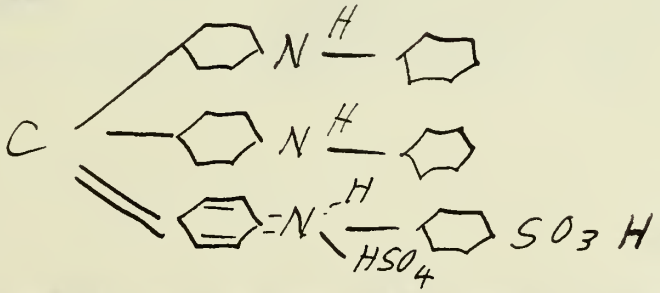
If now more sodium hydroxide is added, the solution becomes weaker and when approximately twice as much sodium hydroxide is added, the solution becomes colorless. The second addition of alkali removes the sulphuric acid from the nitrogen to give the base thusly,



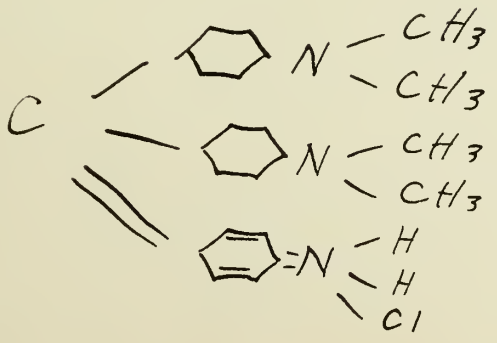
just as sodium hydroxide removes the hydrochloric acid from Fuchsine and gives the base.



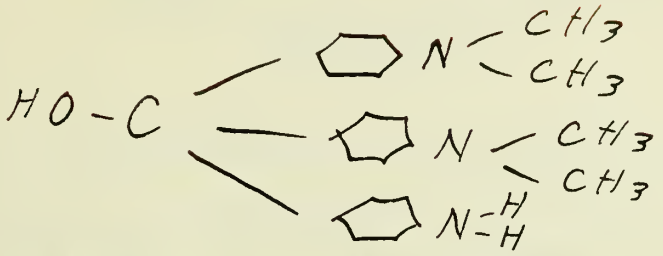
If now sulphuric acid is added, a deep blue precipitate is formed. This is the same compound that was originally formed in the melt.



There is no reason to believe that these phenylated rosanilines should react different than the corresponding alkylated compounds. Thus

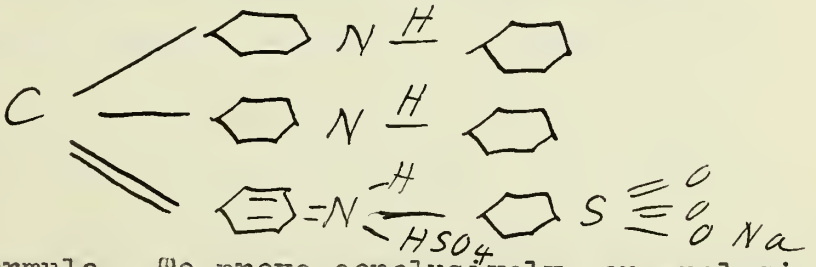


reacts with sodium hydroxide to give



a colorless compound and when this base is treated with hydrochloric or sulphuric acid the original color is restored.

The behavior of Alkali Blue, as well as the general reactions for this type of compounds indicate that



is its true formula. To prove conclusively, an analysis would have to made on the free acid of Alkali Blue.

IV.

Condensation of Diphenylamine.

Experiment I.

50 g. of diphenylamine was dissolved in 100 cc. of ethyl alcohol in a round bottom flask and 11.1 g. of 40% formaldehyde added. The temperature was raised to 60 degrees and 2.5 cc. of 20% hydrochloric acid added. Vigorour reaction took place immediately. Flame was removed but temperature rose to 82 degrees, then gradually sank. At the end of 15 minutes no odor of formaldehyde was present and Fuchsine aldehyde reagent gave negative test. A heavy viscous brown liquid soon settled on the bottom, while the upper layer remained turbulent. The contents were allowed to stand two days, during which time the brown layer became hard. This solid was extracted with three 100 cc. portions of ethyl alcohol. 27 g. of diphenylamine was recovered by precipitating it from the alcohol with water.

The yield of diphenyldiamino diphenylmethane was 7.5 g. =15%.

M. P. 79 to 90 degrees. It did not give a sharp melting point.

The material was dissolved in 50% sulphuric acid and the solution poured into water. The resulting precipitate was dried.

Weight 7g.

M. P. 95 to 100 degrees.

Experiment II.

This experiment was a duplicate of experiment one up to the point of extraction. In this experiment the brown solid was extracted with three 100 cc. portion of ether.

Recovered Diphenylamine 33 g.

Yield 8 g.

M. P. 145 to 150.

The diphenyldiaminodiphenylmethane was recrystalized from benzene.

M. P. 155 to 159.

Oxidation of diphenyldiaminodiphenylmethane.

Experiment III.

A saturated solution containing 10 g. of copper sulphate was poured over 40 g. of sodium chloride and the whole dried. 6 g. of diphenyldiaminodiphenyl methane was dissolved in 3 g. of phenol and 6 g. of diphenylamine and poured over the above salt, heated at 65 to 70 degrees for 24 hours. A very good blue color resulted, but no means of purification could be found.

Sulphonation of Diphenylamine.

Experiment IV.

6 mols of acid to 5 of diphenylamine.

85 g. of diphenylamine was melted in an evaporating dish

dish and 34 cc. of 95% sulphuric acid added. The mass became very viscous and hard to stir and soon turned black after the temperature had been raised to 160 degrees.

Considerable sulphur dioxide was given off. After one hour heating at 160 degrees the mixture was found to be insoluble in alkali and alcohol. The diphenylamine had been oxidized.

Experiment V.

2 mols diphenylamine 1 mol acid.

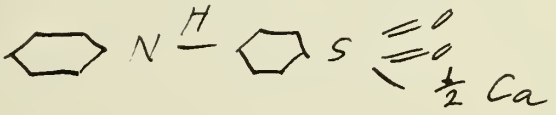
34 g. of diphenylamine was heated to 120 degrees in a 400 cc. beaker and 6 cc. of sulphuric acid (95%) added with stirring.

The color of the mass was light green and it soon became very viscous. Temperature was raised to 150 degrees which caused efforvescence to take place. Melt was held at 150 to 160 degrees for 40 minutes and then poured into 200 cc. of boiling water, neutralized with lime and while solution was hot it was filtered. The residue was extracted and found to contain 14 g. of diphenylamine.

The filtrate was allowed to cool and the crystals of calcium diphenylamine monosulphonate filtered off. It was recrystalized from hot water and some diphenylamine separated on the filterpaper.

Yield 11.3 g of

Equal to 43.8%



Experiment VI.

Experiment five was repeated. Reaction proceeded the same as before.

Yield 9.7 g.

Equal to 29.0%.

Experiment VII.

1 mol of diphenylamine to 1 of acid.

85 g. of diphenylamine was heated in an evaporating dish to 120 degrees and 28 cc. of sulphuric acid (95%) slowly added. At first the liquid solidified but upon the addition of the remainder of the acid it again became liquid. Temperature was raised to 160 degrees and held. Almost immediately sulphur dioxide was given off and the melt turned to a hard black mass. It was insoluble in sodium hydroxide.

Experiment VIII.

1 mol diphenylamine to 1 mol of 50% sulphuric acid.

From this experiment on, a 400 cc. flask provided with an ajitator was used and an oil bath.

43 g. of diphenylamine was melted in a flask and 28 cc. of 50% sulphuric acid added. Temperature raised to 160 degrees; held there for 2 hours and then raised to 180 degrees. The water gradually evaporated out and the sulphonation then proceeded as in experiment seven. Sulphur di-

oxide was given off. The mass was boiled up with sodium hydroxide solution. A green powder resulted which had a M.P. over 250 degrees.

Experiment IX.

1 mol diphenylamine to 1 mol of 75% sulphuric acid.

43 g. of diphenylamine was melted and 14 cc. of acid plus 4.7 cc. of water added. The reaction and results were the same as in experiment eight.

Experiment X.

2 mols diphenylamine to 1 of acid.

85 g. of diphenylamine was melted in the flask and 28 cc. of sulphuric acid slowly added. Considerable frothing took place. Temperature was raised to 160 to 170 degrees and held there for six hours. Melt was poured into hot water and neutralized with lime. Solution allowed to partially cool to 45 degrees and filtered. Upon cooling the calcium diphenylamine monosulphonate crystalized out.

Yield 32 g. equal to 46.7% theoretical.

Experiment XI.

Experiment ten was repeated holding the temperature between 180 and 190 degrees. After about four hours heating the temperature accidentally rose to 235 to 240 degrees. Sulphur dioxide was evolved and the melt turned hard and black the same as when too large a proportion of acid was used.

Experiment XII.

Experiment ten was repeated and the temperature held at 180 to 190 degrees for 16 hours. At the end the melt had a very light pink color. It was poured into hot water limed and the diphenylamine and excess lime filtered off by partial cooling.

Yield of diphenylamine monsulphonate 37 g. equal to 56.2%

Recovered diphenylamine 34.2 g. equal to 42%.

Experiment XIII.

Experiment twelve was repeated but this time the sulphonation melt was poured into hot water and sodium carbonate added till neutral. Solution was cooled and the unreacted diphenylamine filtered off, 38 g. equal to 44.7 recovered.

The sodium siphenylamine monosulphonate was evaporated down to dryness and used in a condensation experiment.

Yield 45 g.

Condensation of Calcium diphenylamine monosulphonate.

Experiment XIV.

20 g. of the calcium salt was dissolved in 100 cc. of water and 5 cc. of 40% formaldehyde added. Solution was heated on water bath till dryness (4 hours).

Residue was a grey soluble solid.

Yield 19 g. equal to 93%.

Experiment XV.

This experiment was run the same as XIV. except that 1 cc. of 20% hydrochloric acid was added the solution to catalyze the reaction. As evaporation took place the solution became brown and viscous. At the end the residue was hard and dark brown and insoluble in water.

Various methods of oxidation were attempted but no color could be obtained. The hydrochloric acid proved very detrimental to the condensation.

Experiment XVI.

This was run the same as experiment XIV. except that a few drops of sodium hydroxide was added to make it distinctly alkaline. The residue was a very light grey and water soluble. That it was only a partial condensation was shown when it was oxidized to the color.

Yield 19.5 g. equal to 95.6%

Oxidation to the Dye.

Experiment XVII.

10 g. of the condensation product was dissolved in 50 cc. of water. 5 cc. of concentrated sulphuric acid and 5 g. of calcium diphenylamine monosulphonate added, then a solution containing 10 g. of potassium chlorate. The solution first became blue and then very quickly changed to a black. The oxidation could not be controlled.

Experiment VIII.

Carried out the same as experiment XVII. but potassium dichromate was used in place of the potassium chlorate.

Results were the same as in preceeding experiment. Lowering the amount of acid and oxidizing agent did not change the results.

ExperimentXIX.

10 g. of the condensation product was dissolved in 50 cc. of water and 5 g. of calcium diphenylamine mono sulphonate added, then 5 cc. of hydrochloric acid. The solution was cooled and 15 g. of powdered lead peroxide slowly added with agitation. Solution first turned light green then became darker and darker till a deep blue color was reached. Ammonium carbonated was added the soluble salt of the dye filtered from the lead sludge. Resulting dye was a very green shade blue and dyed silk and wool a very good shade.

Experiment XX.

Run the same as experiment XIX. except that 20 cc. of glacial acetric acid was used in place of the hydrochloric. The solution turned brown and then a very dark brown, as a final product. Smaller amounts of acetic acid gave practically the same results.

Experiment XI.

Run the same as experiment XIX. except 5 cc. of concentrated sulphuric acid was used in place of the hydrochloric acid. The reaction proceeded much slower than when hydrochloric acid was used. No blue color developed for five hourse. Reaction was

allowed to proceed 36 hours by which time it was assumed complete. The shade was a little greener than when hydrochloric acid was used.

Ammonium carbonate was added and the resulting dye filtered and evaporated to dryness.

V.

Summary.

Two mols of diphenylamine to one of sulphuric acid was found to be the best ratio for the production of diphenylamine monosulphonic acid. Temperature should be 170 to 180 degrees.

Condensation of calcium diphenylamine monosulphorate with formaldehyde takes place best in a neutral solution and with an excess of the latter.

The most satisfactory oxidizing agent was found to be lead peroxide with hydrochloric acid.

References:

Diphenylamine monosulphonic acid

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Berichte	" 6.	" 1513		

Diphenyldiaminodiphenylmethane

Winthers	Volume II	" 48	"	" 58,072

Water Blue

Winthers	" II	" 149	"	" 73,092

Preparation para Fuchsine

Friedlander	Volume III (1890-94)	" 112

Diaminodiphenyl Methane

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Anhydro formaldehydeanilin

Berichte	Volume XVIII	" 3309

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